

=> d his

(FILE 'HOME' ENTERED AT 08:23:42 ON 18 MAR 2010)

FILE 'REGISTRY' ENTERED AT 08:23:53 ON 18 MAR 2010

L1 STRUCTURE UPLOADED
L2 0 S L1
L3 13 S L1 FULL
L4 STRUCTURE UPLOADED
L5 23 S L4
L6 14539 S L4 FULL
L7 0 S L3 AND L6

=> d que 17 stat

L1 STR

P⁻____
|
F

Structure attributes must be viewed using STN Express query preparation.

L3 13 SEA FILE=REGISTRY SSS FUL L1
L4 STR

Hy-----[CH-----CH]₁₋₁₀CH-----Cy

Structure attributes must be viewed using STN Express query preparation.

L6 14539 SEA FILE=REGISTRY SSS FUL L4
L7 0 SEA FILE=REGISTRY ABB=ON PLU=ON L3 AND L6

=> fil capl

FILE 'CAPLUS' ENTERED AT 08:27:21 ON 18 MAR 2010

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FILE COVERS 1907 - 18 Mar 2010 VOL 152 ISS 12

FILE LAST UPDATED: 17 Mar 2010 (20100317/ED)

REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2009

USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2009

CAPLUS now includes complete International Patent Classification (IPC) reclassification data for the first quarter of 2010.

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This file contains CAS Registry Numbers for easy and accurate substance identification.

'FIONA' IS DEFAULT FORMAT FOR 'CAPLUS' FILE

=> s 13

L8 6 L3

=> d 1-6 ibib iabs hitstr

L8 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN

ACCESSION NUMBER: 2008:1319707 CAPLUS

DOCUMENT NUMBER: 149:576715

TITLE: Competing C-F Activation Pathways in the Reaction of Pt(0) with Fluoropyridines: Phosphine-Assistance versus Oxidative Addition

AUTHOR(S): Nova, Ainara; Erhardt, Stefan; Jasim, Naseralla A.; Perutz, Robin N.; Macgregor, Stuart A.; McGrady, John E.; Whitwood, Adrian C.

CORPORATE SOURCE: Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

SOURCE: Journal of the American Chemical Society (2008), 130(46), 15499-15511

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 149:576715

ABSTRACT:

A survey of computed mechanisms for C-F bond activation at the 4-position of pentafluoropyridine by the model zero-valent bis-phosphine complex, [Pt(PH₃)(PH₂Me)], reveals three quite distinct pathways leading to square-planar Pt(II) products. Direct oxidative addition leads to cis-[Pt(F)(4-C₅NF₄)(PH₃)(PH₂Me)] via a conventional 3-center transition state. This process competes with two different phosphine-assisted mechanisms in which C-F activation involves F transfer to a P center via novel 4-center transition states. The more accessible of the two phosphine-assisted processes involves concerted transfer of an alkyl group from P to the metal to give a Pt(alkyl)(fluorophosphine), trans-[Pt(Me)(4-C₅NF₄)(PH₃)(PH₂F)], analogs of which were observed exptl. The 2nd phosphine-assisted pathway sees F transfer to one of the phosphine ligands with formation of a metastable metallophosphorane intermediate from which either alkyl or F transfer to the metal is possible. Both Pt-fluoride and Pt(alkyl)(fluorophosphine) products are therefore accessible via this route. The calcs. highlight the central role of metallophosphorane species, either as intermediates or transition states, in aromatic C-F bond activation. The similar computed barriers for all three processes suggest that Pt-fluoride species should be accessible. This is confirmed exptl. by the reaction of [Pt(PR₃)₂] species (R = iso-Pr (iPr), cyclohexyl (Cy), and cyclopentyl (Cyp)) with 2,3,5-trifluoro-4-(trifluoromethyl)pyridine to give cis-[Pt(F){2-C₅NHF₂(CF₃)}(PR₃)₂]. These species subsequently convert to the trans-isomers, either thermally or photochem. The crystal structure of cis-[Pt(F){2-C₅NHF₂(CF₃)}(PiPr₃)₂] shows planar coordination at Pt with r(F-Pt) = 2.029(3) Å and P(1)-Pt-P(2) = 109.10(3)°. The crystal structure of trans-[Pt(F){2-C₅NHF₂(CF₃)}(PCyp₃)₂] shows standard square-planar coordination at Pt with r(F-Pt) = 2.040(19) Å.

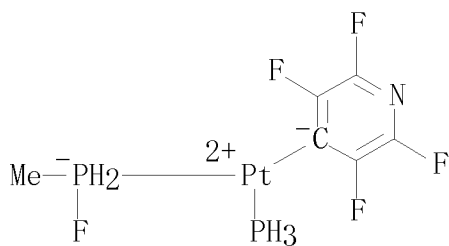
IT 1083009-53-3

RL: PRP (Properties)

(DFT-calculated optimized geometry and energy; oxidative addition reaction of trifluoro(trifluoromethyl)pyridine with Pt bisphosphine complex via C-F bond activation)

RN 1083009-53-3 CAPLUS

CN Platinum, (fluoromethylphosphoranyl)(phosphine)(2,3,5,6-tetrafluoro-4-pyridinyl)-, stereoisomer (CA INDEX NAME)



OS. CITING REF COUNT: 10

THERE ARE 10 CAPLUS RECORDS THAT CITE THIS
RECORD (10 CITINGS)

REFERENCE COUNT: 72

THERE ARE 72 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN

ACCESSION NUMBER: 2008:1319649 CAPLUS

DOCUMENT NUMBER: 150:5876

TITLE: Computational Study of the Reaction of C₆F₆ with
[IrMe(PEt₃)₃]: Identification of a Phosphine-Assisted
C-F Activation Pathway via a Metallophosphorane
Intermediate

AUTHOR(S): Erhardt, Stefan; Macgregor, Stuart A.

CORPORATE SOURCE: School of Engineering and Physical Sciences,
Heriot-Watt University, Edinburgh, EH14 4AS, UKSOURCE: Journal of the American Chemical Society (2008),
130(46), 15490-15498

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 150:5876

ABSTRACT:

D. functional theory calcns. were used to model the reaction of C₆F₆ with [IrMe(PEt₃)₃], which proceeds with both C-F and P-C bond activation to yield trans-[Ir(C₆F₅)(PEt₃)₂(PEt₂F)], C₂H₄, and CH₄. Using a model species, trans-[IrMe(PH₃)₂(PH₂Et)], a low-energy mechanism involving nucleophilic attack of the electron-rich Ir metal center at C₆F₆ with displacement of fluoride was identified. A novel feature of this process is the capture of fluoride by a phosphine ligand to generate a metallophosphorane intermediate [Ir(C₆F₅)(Me)(PH₃)₂(PH₂EtF)]. These events occur in a single step via a 4-centered transition state, in a process that the authors have termed phosphine-assisted C-F activation. Alternative mechanisms based on C-F activation via concerted oxidative addition or electron-transfer processes proved less favorable. From the metallophosphorane intermediate the formation of the final products can be accounted for by facile Et group transfer from P to Ir followed by β-H elimination of ethene and reductive elimination of methane. The interpretation of phosphine-assisted C-F activation in terms of nucleophilic attack is supported by the reduced activation barriers computed with the more electron-rich model reactant trans-[IrMe(PMe₃)₂(PMe₂Et)] and the higher barriers found with lesser fluorinated arenes. Reactivity patterns for a range of fluoroarenes indicate the dominance of the presence of ortho-F substituents in promoting phosphine-assisted C-F activation, and an anal. of the charge distribution and transition state geometries indicates that this process is controlled by the strength of the Ir-aryl bond that is being formed.

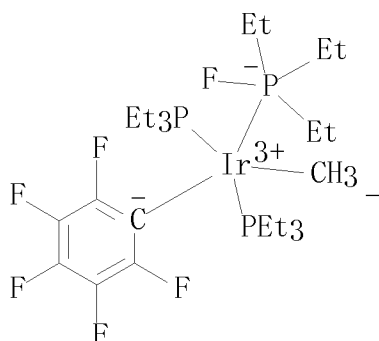
IT 1083252-62-3

RL: PRP (Properties)

(DFT calcn. of the reaction of hexafluorobenzene with
methyltris(triethylphosphine)iridium to identify a phosphine-assisted
C-F activation pathway via a metallophosphorane intermediate)

RN 1083252-62-3 CAPLUS

CN Iridium, methyl(2,3,4,5,6-
pentafluorophenyl)(triethylfluorophosphoranyl)bis(triethylphosphine)-,
(SP-5-34)- (CA INDEX NAME)



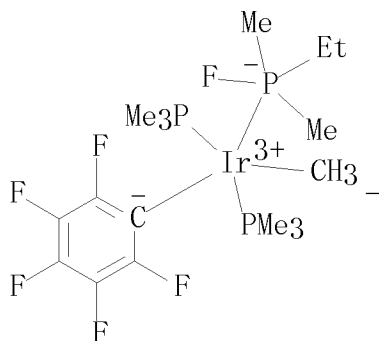
IT 1083252-89-4 1083252-95-2 1083253-01-3

RL: PRP (Properties)

(calculated optimized geometry and energy; DFT calcn. of the reaction of hexafluorobenzene with methyltris(triethylphosphine)iridium to identify a phosphine-assisted C-F activation pathway via a metallophosphorane intermediate)

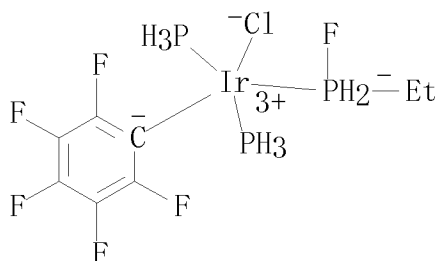
RN 1083252-89-4 CAPLUS

CN Iridium, (ethylfluorodimethylphosphoranyl)methyl (2,3,4,5,6-pentafluorophenyl)bis(trimethylphosphine)-, (SP-5-34)- (CA INDEX NAME)



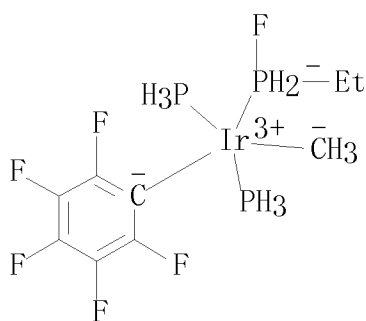
RN 1083252-95-2 CAPLUS

CN Iridium, chloro(ethylfluorophosphoranyl-κP) (2,3,4,5,6-pentafluorophenyl)bis(phosphine)-, (SP-5-42)- (CA INDEX NAME)



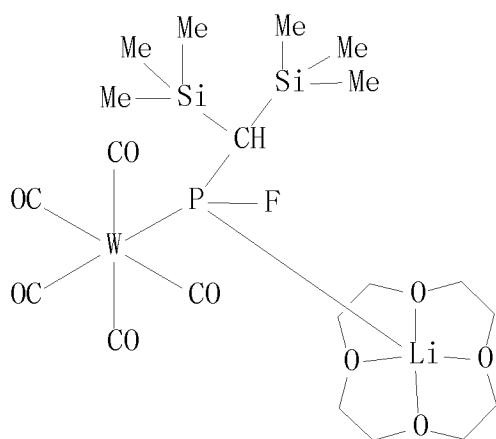
RN 1083253-01-3 CAPLUS

CN Iridium, (ethylfluorophosphoranyl-κP)methyl (2,3,4,5,6-pentafluorophenyl)bis(phosphine)-, (SP-5-34)- (CA INDEX NAME)



OS. CITING REF COUNT:	8	THERE ARE 8 CAPLUS RECORDS THAT CITE THIS RECORD (8 CITINGS)
REFERENCE COUNT:	96	THERE ARE 96 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN
 ACCESSION NUMBER: 2008:547396 CAPLUS
 DOCUMENT NUMBER: 149:166560
 TITLE: Isolation of the first Li/halogen phosphinidenoid transition-metal complex
 AUTHOR(S): Oezbolat, Aysel; von Frantzius, Gerd; Hoffbauer, Wilfried; Streubel, Rainer
 CORPORATE SOURCE: Institut fuer Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universitaet Bonn, Bonn, 53121, Germany
 SOURCE: Dalton Transactions (2008), (20), 2674-2676
 CODEN: DTARAF; ISSN: 1477-9226
 PUBLISHER: Royal Society of Chemistry
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 149:166560
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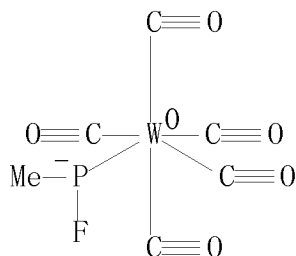


I

ABSTRACT:

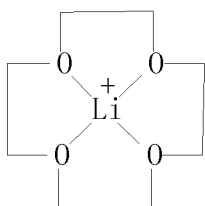
The 1st Li/halogen phosphinidenoid transition-metal complex (I) was isolated and characterized as well as the reporting of low-temperature solution NMR, MAS NMR expts., DFT structures and calculated NMR chemical shifts.

IT 1035693-81-2 1035693-82-3
 RL: PRP (Properties)
 (mol. structure from DFT calcs. as model for tungsten carbonyl lithium
 fluorine phosphinidenoid complex)
 RN 1035693-81-2 CAPLUS
 CN Lithium(1+), (1,4,7,10-tetraoxacyclododecane-
 κO1, κO4, κO7, κO10)-, (T-4)-,
 pentacarbonyl (P-methylphosphinous fluoridato-κP) tungstate(1-) (1:1)
 (CA INDEX NAME)
 CM 1
 CRN 1035693-80-1
 CMF C6 H3 F O5 P W
 CCI CCS

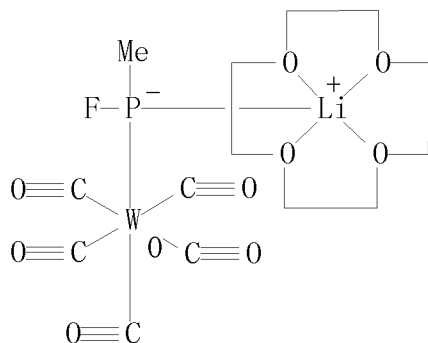


CM 2

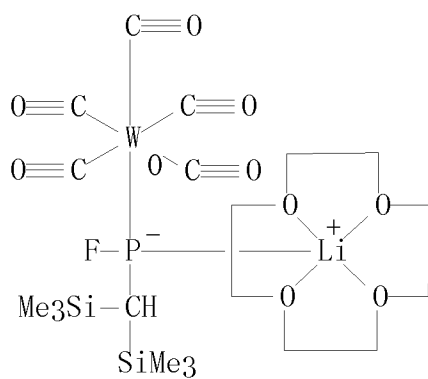
CRN 57448-31-4
 CMF C8 H16 Li 04
 CCI CCS



RN 1035693-82-3 CAPLUS
 CN Lithium, [μ -(P-methylphosphinous
 fluoridato- κ P: κ P)] (pentacarbonyltungsten) (1, 4, 7, 10-
 tetraoxacyclododecane- κ 01, κ 04, κ 07, κ 010)- (CA
 INDEX NAME)



IT 1035693-79-8P
 RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
 (preparation and optimized mol. structure from DFT calcns. of)
 RN 1035693-79-8 CAPLUS
 CN Lithium, [μ -[P-[bis(trimethylsilyl)methyl]phosphinous
 fluoridato- κ P: κ P)] (pentacarbonyltungsten) (1, 4, 7, 10-
 tetraoxacyclododecane- κ 01, κ 04, κ 07, κ 010)- (CA
 INDEX NAME)



REFERENCE COUNT:

30

THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 4 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN

ACCESSION NUMBER: 2007:631330 CAPLUS

DOCUMENT NUMBER: 148:538342

TITLE: Gas phase FT ICR investigation of the production of phosphoranides and ion chemistry of tris(trifluoromethyl)phosphine

AUTHOR(S): Kanawati, B.; Wanczek, K. P.

CORPORATE SOURCE: Department of Physical and Inorganic Chemistry, University of Bremen, Bremen, Germany

SOURCE: International Journal of Mass Spectrometry (2007), 264(2-3), 164-174

CODEN: IMSPF8; ISSN: 1387-3806

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

ABSTRACT:

In a long cylindrical ICR cell the ion chemical of tris(trifluoromethyl)phosphine was studied. The only major neg. primary ion, produced by dissociative electron attachment is the phosphide ion (CF₃)₂P⁻, which reacts at elevated kinetic energy with the neutral mols. at 2 + 10⁻⁷ m bar to produce three phosphoranides: CF₃PF₃⁻, (CF₃)₂PF₂⁻, and (CF₃)₃PF⁻. Simultaneously, three minor ions CF₃⁻, F⁻, and C₂F₃⁻ are formed by self-collision-induced dissociation. Ion-mol. reactions between CF₃⁻ and (CF₃)₃P also were studied. Pos. ions form phosphonium ions and a diphosphonium product ion, (CF₃)₂P-P(CF₃)₃⁺, whereas no P-P bond is observed with neg. ions. All the structures and reaction pathways were studied theor. with the aid of DFT calcns. The results are in excellent agreement with the expts. The electron affinity of tris(trifluoromethyl)phosphine as EA((CF₃)₃P) = 22.6 kcal/mol was calculated

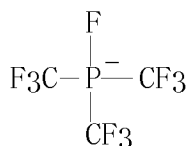
IT 1023674-90-9

RL: PRP (Properties)

(DFT-calculated optimized geometry and energy; gas phase FT ICR investigation of the production of phosphoranides and ion chemical of tris(trifluoromethyl)phosphine)

RN 1023674-90-9 CAPLUS

CN Phosphorane, fluorotris(trifluoromethyl)-, ion(1-) (CA INDEX NAME)



OS.CITING REF COUNT: 3 THERE ARE 3 CAPLUS RECORDS THAT CITE THIS RECORD (3 CITINGS)

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 5 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN

ACCESSION NUMBER: 2006:208544 CAPLUS

DOCUMENT NUMBER: 146:62790

TITLE: Splitting the phosphorus bridge of
7-phosphanorbornadiene complexes by fluoride ion

AUTHOR(S): Compain, Carine; Mathey, Francois

CORPORATE SOURCE: UCR-CNRS Joint Research Chemistry Laboratory,
Department of Chemistry, University of California
Riverside, Riverside, CA, USA

SOURCE: Zeitschrift fuer Anorganische und Allgemeine Chemie
(2006), 632(3), 421-424

CODEN: ZAACAB; ISSN: 0044-2313

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:62790

ABSTRACT:

The reaction of fluoride ion with 7-phosphanorbornadiene P-W(CO)₅ complexes yields fluorophosphido complexes which, in turn, can attack a second mol. of 7-phosphanorbornadiene to give a fluorobiphosphine complex. The corresponding anion displays a huge P-P coupling. The structure of the anionic chromium analog has been investigated by DFT calcs. The P-P bond is relatively short at 2.20 Å and displays a huge polarity suggesting an interesting chemical When the 7-phosphanorbornadiene P-substituent is 2-chloroethyl, the attack of the fluoride ion is followed by a cyclization and a reductive dimerization leading to the first known biphosphirane complex.

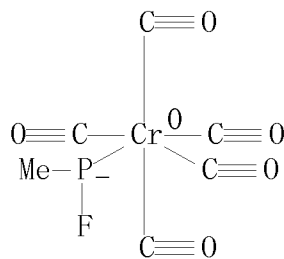
IT 916771-12-5

RL: PRP (Properties)

(mol. structure calcn.; cleavage of phosphorus bridge of
phosphanorbornadiene tungsten carbonyl complex by fluoride ion)

RN 916771-12-5 CAPLUS

CN Chromate(1-), pentacarbonyl(methylphosphinous fluoridato-κP)-,
(OC-6-22)- (CA INDEX NAME)



OS. CITING REF COUNT: 5 THERE ARE 5 CAPLUS RECORDS THAT CITE THIS RECORD
(5 CITINGS)

REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2010 ACS on STN

ACCESSION NUMBER: 1980:549603 CAPLUS

DOCUMENT NUMBER: 93:149603

ORIGINAL REFERENCE NO.: 93:23831a, 23834a

TITLE: Hydroxyphosphorane intermediates in substitution reactions at phosphorus in acyclic phosphonofluoridates: evidence from nuclear magnetic resonance

AUTHOR(S): Granoth, Itshak; Segall, Yoffi; Waysbort, Daniel; Shirin, Ezra; Leader, Haim

CORPORATE SOURCE: Israel Inst. Biol. Res., Ness-Ziona, 70400, Israel

SOURCE: Journal of the American Chemical Society (1980), 102(13), 4523-5

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

ABSTRACT:

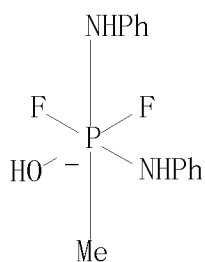
MeP(O)F₂ (I) reacted with RNH₂ (R = Ph, Bu) to give MeP(O)FNHR (II) in surprisingly slow reactions. ¹H and ³¹P NMR evidence is consistent with formation of a small concentration of phosphorane intermediate MePF₂(O⁻)NH₂R⁺ (III), which is in equilibrium with I and participates in an F-exchange process. The equilibrium involving I and III (R = Bu) is established by starting from either I and BuNH₂ or II (R = Bu) and anhydrous HF.

IT 74963-93-2P

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 74963-93-2 CAPLUS

CN Phosphate(1-), difluorohydroxymethylbis(benzenaminato)-, hydrogen (9CI)
(CA INDEX NAME)



OS.CITING REF COUNT: 1 THERE ARE 1 CAPLUS RECORDS THAT CITE THIS RECORD
(1 CITINGS)

=> d his full

(FILE 'HOME' ENTERED AT 08:23:42 ON 18 MAR 2010)

FILE 'REGISTRY' ENTERED AT 08:23:53 ON 18 MAR 2010

L1 STRUCTURE UPLOADED
 D
L2 0 SEA SSS SAM L1
L3 13 SEA SSS FUL L1
L4 STRUCTURE UPLOADED
 D
L5 23 SEA SSS SAM L4
L6 14539 SEA SSS FUL L4
L7 0 SEA ABB=ON PLU=ON L3 AND L6
 D QUE L7 STAT

FILE 'CAPLUS' ENTERED AT 08:27:21 ON 18 MAR 2010

L8 6 SEA ABB=ON PLU=ON L3
 D 1-6 IBIB IABS HITSTR

FILE HOME

FILE REGISTRY

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DICTIONARY FILE UPDATES: 17 MAR 2010 HIGHEST RN 1211109-76-0

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FILE COVERS 1907 - 18 Mar 2010 VOL 152 ISS 12

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 REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2009
 USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2009

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FULL ESTIMATED COST	35.86	421.12
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-5.10	-5.10

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(FILE 'HOME' ENTERED AT 08:23:42 ON 18 MAR 2010)

FILE 'REGISTRY' ENTERED AT 08:23:53 ON 18 MAR 2010

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L1      STRUCTURE UPLOADED
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L3      13 SEA SSS FUL L1
L4      STRUCTURE UPLOADED
        D
L5      23 SEA SSS SAM L4
L6      14539 SEA SSS FUL L4
L7      0 SEA ABB=ON PLU=ON L3 AND L6
        D QUE L7 STAT
  
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FILE 'CAPLUS' ENTERED AT 08:27:21 ON 18 MAR 2010

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L8      6 SEA ABB=ON PLU=ON L3
        D 1-6 IBIB IABS HITSTR
  
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FILE 'CAPLUS' ENTERED AT 09:31:35 ON 18 MAR 2010

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L9      0 SEA ABB=ON PLU=ON FLUOROALKYLPHOSPHATE AND (POLYMETHINE OR
        ?CYANINE?)
L10     0 SEA ABB=ON PLU=ON FLUOROALKYLPHOSPHATE AND DYE?
L11     27 SEA ABB=ON PLU=ON FLUOROALKYLPHOSPHATE
L12     0 SEA ABB=ON PLU=ON L11 AND DYES/SC
  
```

FILE HOME

FILE REGISTRY

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STRUCTURE FILE UPDATES: 17 MAR 2010 HIGHEST RN 1211109-76-0
DICTIONARY FILE UPDATES: 17 MAR 2010 HIGHEST RN 1211109-76-0

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<http://www.cas.org/support/stngen/stndoc/properties.html>

FILE CAPLUS

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REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2009
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2009

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This file contains CAS Registry Numbers for easy and accurate
substance identification.

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COST IN U. S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	19.17	440.79
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	0.00	-5.10

SESSION WILL BE HELD FOR 120 MINUTES
STN INTERNATIONAL SESSION SUSPENDED AT 09:34:54 ON 18 MAR 2010